

# Polymeric Species of Pu in Low Ionic Strength Media

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### **Introduction**

The U.S. Government has declared that approximately 50 tons of plutonium is surplus to U.S. needs and should be set aside for eventual disposition. The U.S. is currently following a dual path for the disposition of this plutonium: immobilization and irradiation of mixed-oxide fuel.<sup>1</sup>

Some fraction of this plutonium material that is undesirable for use in mixed-oxide fuel will be immobilized in a titanate ceramic and disposed of in a geologic repository for high level waste. The remainder of Pu will be fabricated into mixed-oxide fuel and irradiated in domestic light-water reactors. The resulting spent fuel would also be disposed of in a geologic repository for high level waste. The proposed U.S. repository would be at the Yucca Mountain site in Nevada.

Plutonium present in the disposal forms, either ceramics or spent fuel, must remain isolated from the biosphere over the geologic repository regulatory performance period, which is currently 10,000 years. Contamination of the biosphere could result from slow dissolution of the disposal forms followed by transport of the dissolution products into the biosphere by flowing ground water. Measurable amounts of apparently soluble plutonium can be released if plutonium dioxide is exposed to water under some conditions.<sup>2</sup> Furthermore, recent studies in Nevada near the Yucca Mountain Site revealed that plutonium, associated with

the colloidal fraction of the groundwater, was detected over a kilometer from its source within 30 years after it was placed underground for a nuclear weapons testing.<sup>3</sup> It was not clear whether plutonium was transported as an intrinsic plutonium colloid or as plutonium sorbed onto colloidal clay or zeolite particles.

### **Description of work and results**

The formation of plutonium colloids was studied in a surrogate Yucca Mountain groundwater similar in composition to water from well J-13 at the Nevada Test Site. Experiments were conducted at several pHs under an air atmosphere at 25 °C. Pu(V) is the dominant oxidation state of plutonium in water at atmospheric oxygen fugacity<sup>2</sup>. Solutions containing  $10^{-4}$  M Pu(V) and  $10^{-6}$  M Pu(V) were produced in J-13 surrogate at pH 1, 3, 6, 8, and 11, and the plutonium solutions were monitored for several months. Aliquots were taken periodically and analyzed using ultrafiltration and liquid scintillation spectrometry. Several times during the experiment, the plutonium oxidation state distribution was determined using solvent extraction techniques.

The results show that the Pu(V) oxidation state dominated under conditions relevant to natural systems. For both plutonium concentrations, 10 to 25% of the plutonium in every sample was present as a non-extractable, suspended form of plutonium that passed through a 0.01-micron filter. We infer that this material was a polymeric form of plutonium.

The plutonium species distribution under the conditions of the experiment was calculated using the Geochemist's Workbench package.<sup>4</sup> The calculated and experimentally determined total concentrations of dissolved plutonium were in

reasonable agreement only if one accounts for the polymeric plutonium. There are no polymeric plutonium species represented in the thermodynamic database used to model the experiments.<sup>5</sup> The fact that polymeric species were present in significant quantities in our experiments raises the question of their long-term stability and their possible role in long-term plutonium transport in the underground environment of a geologic repository. This work is focused on collecting data to address this possible transport role of plutonium as a colloid.

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